# Continuum wave functions and phase shifts for the one-electron state of the Coulomb two-center problem

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Electronic continuum angular and radial wave functions are represented in a compact form by expansions over spherical harmonics and the Legendre functions of the first kind, respectively, with separated exponents. Particularly for the continuum radial case, the phase shift is expressed through the characteristic exponent by a formula that generalizes previous asymptotic analytic expressions for small and large intercenter distances.

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## I. INTRODUCTION

There have been numerous studies of the Coulomb one-electron two-center problem. Most of these concern bound states and are based on the use of continued fractions [1] or matrix methods [2] or power series and associated Legendre expansion series with use of recurrence relation properties [3] or by power series only [4], etc. For the continuum states, additional difficulties arise when trying to solve analytically the Schrödinger equation describing the motion of the electron in the field of the two fixed nuclei $A$ and $B$ with charges $Z_A$ and $Z_B$. Most authors have obtained the electronic continuum wave functions by numerical methods [5–7] but, so far, few of them have been interested in finding analytic solutions to the problem. Greenland and Greiner [8] have presented several mathematical closed-form solutions in the entire complex plane but determined the phase shifts by using different recurrence relations and corrected errors in a preceding paper [9]. Later, Abramov and Slavyanov [10] and Abramov *et al.* [11] proposed an asymptotic expansion for the phase shifts in the united-atom approximation in terms of the parameter $\nu$, called the characteristic exponent [8]. For large intercenter distances, they used the asymptotic formula of Komarov, Ponomarev, and Slavyanov [12]. In this work, the analytic approach is reinvestigated. Closed-form solutions are obtained by choosing the convenient basis functions which lead to a pair of three-term recurrence relations for the separated angular and radial Schrödinger equations, respectively. Particularly, in the radial case, the phase shifts are determined through an analytic expression in terms of $\nu$ for the whole range of the intercenter distance. For illustration, application to the $s\sigma$ state of $H_2^+$ is considered and comparative values of the phase shift by use of the analytic formula with those found by numerical procedures [6,7] are presented for the $s\sigma$, $p\sigma$, and $p\pi$ states of $H_eH^{2+}$. All calculations are performed in atomic units.

## II. GENERAL CONSIDERATIONS

It is well known that the equation of motion of one electron moving in the field of two fixed nuclei $A$ and $B$ and distant $r_A$ and $r_B$ from $A$ and $B$ is separable in prolate spheroidal coordinates:

$$\begin{aligned}&\mu=(r_A-r_B)/R\ ,\quad 1\le\mu\le+1\ ,\\&\lambda=(r_A+r_B)/R\ ,\quad 1\le\lambda<\infty,\quad 0\le\varphi\le2\pi\ .\end{aligned}\tag{1}$$

This separation leads to the angular and radial forms

$$\left\{\frac{d}{d\mu}(1-\mu^2)\frac{d}{d\mu}-\frac{m^2}{1-\mu^2}+R(Z_A-Z_B)\mu-p^2\mu^2+A\right\}M(\mu,\varphi)=0\ ,\tag{2}$$

$$\left\{\frac{d}{d\lambda}(\lambda^2-1)\frac{d}{d\lambda}-\frac{m^2}{\lambda^2-1}+R(Z_A+Z_B)\lambda+p^2\lambda^2-A\right\}\Lambda(\lambda)=0\ .\tag{3}$$

For the continuum states, the energy parameter $p$ is defined by $p^2=ER^2/2$ where $E=K^2/2$ is the energy for an electron in a state with momentum $K$. Then $p=KR/2$; $m$ is the magnetic quantum number and $A$ is the separation constant representing the eigenvalue of another constant of motion related to the total angular momentum and to the Runge-Lenz vector [13]. $M(\mu,\varphi)$ and $\Lambda(\lambda)$ are the angular and radial regular solutions of Eqs. (2) and (3), respectively. The wave function is given by

$$\phi_{l|m|}(K,R;\mu,\lambda,\varphi)=N_{l|m|}(K,R)M(\mu,\varphi)\Lambda(\lambda)\ ,\tag{4}$$

where $N_{l|m|}(K,R)$ is the normalization constant, and $l$ ($l=|m|+q$, $q=0,1,2,\ldots$) represents a quantum number corresponding to the azimuthal quantum number in the

 

spherically symmetric case, i.e., the united-atom-limit angular momentum number.

## III. ANGULAR EQUATION

There is no difficulty in solving Eq. (2). We shall recall here the process used to obtain the separation constant and the angular functions $M(\mu,\varphi)$.

### A. Expansion and recurrence relations

An appropriate regular expansion for $M(\mu,\varphi)$ is

$$M(\mu,\varphi)=\mathcal{N}_{l|m|}e^{\pm ip\mu}\sum_{n=|m|} g_n^{\pm}Y_n^m(\eta,\varphi)\ , \tag{5}$$

where the spherical harmonics $Y_n^m(\eta)$ are defined in terms of the associated Legendre polynomials $P_n^m(\mu)$ as

$$Y_n^m(\eta,\varphi)=(-1)^m\left\{\frac{2n+1}{4\pi}\frac{\Gamma(n+1-m)}{\Gamma(n+1+m)}\right\}^{1/2}\times P_n^m(\cos\eta)e^{im\varphi}\ .$$

The angle $\eta$ ($\mu=\cos\eta$) is restricted to the range $0\le\eta\le\pi$.

The constant $\mathcal{N}_{l|m|}$ is chosen so that $\int M(\mu,\varphi)M^*(\mu,\varphi)d\tau=1$ with $d\tau=\sin\eta\,d\eta\,d\varphi$. The substitution of Eq. (5) into Eq. (2) leads to the following three-term recurrence relation for the $g_n^{\pm}$ coefficients:

$$\begin{aligned}
&a_n^{\pm}g_{n-1}^{\pm}+b_ng_n^{\pm}+c_n^{\pm}g_{n+1}^{\pm}=0\ ,\\
&a_n^{\pm}=[R(Z_A-Z_B)\pm 2ipn]\times\left\{\frac{(n^2-m^2)}{(2m-1)(2n+1)}\right\}^{1/2}\ ,\\
&b_n=p^2-A+n(n+1)\ ,\\
&c_n^{\pm}=[R(Z_A-Z_B)\mp 2ip(n+1)]\times\left\{\frac{(n+1)^2-m^2}{(2n+1)(2n+3)}\right\}^{1/2}\ ,
\end{aligned} \tag{6}$$

with the boundary condition $g_{|m|-1}^{\pm}=0$.

We can symmetrize the matrix whose elements are the coefficients in Eq. (6) by setting

$$\begin{aligned}
g_n^{\pm}&=e^{\mp i(\pi/2)n}\left\{\frac{\Gamma(n+1\mp is)}{\Gamma(n+1\pm is)}\right\}^{1/2}C_n\\
&=e^{i[\mp(\pi/2)n+\arg\Gamma(n+1\mp is)]}C_n\ ,
\end{aligned} \tag{7}$$

where

$$s=\frac{R(Z_A-Z_B)}{p}=\frac{Z_A-Z_B}{K}\ .$$

The new coefficients $C_n$ satisfy the equation

$$\begin{aligned}
&u_nC_{n-1}+b_nC_n+u_{n+1}C_{n+1}=0\ ,\\
&u_n=-2p\left\{\frac{(n^2-m^2)(n^2+s^2)}{(2n-1)(2n+1)}\right\}^{1/2}\ ,
\end{aligned} \tag{8}$$

where $b_n=p^2-A+n(n+1)$.

Equation (8) may be considered as an infinite set of homogeneous equations for the $C_n$ coefficients. For this set to be compatible, the determinant of the associated matrix $[\mathcal{M}-\mathcal{I}A]$ must be equal to zero,

$$\det[\mathcal{M}-\mathcal{I}A]=0\ . \tag{9}$$

The eigenvalues of $[\mathcal{M}]$ are the separation constants $A$ (i.e., $A_{l|m|}$), which must be labeled by $l=|m|+q$, $q=0,1,2,\ldots$. $\mathcal{I}$ is the identity matrix. The matrix $[\mathcal{M}]$ being symmetric, all the $A_{l|m|}$ eigenvalues are real, and since its elements are real all the $C_n$ coefficients can be considered as real. Hence

$$M(\mu,\varphi)=e^{\pm ip\mu}\times\sum_{n=|m|}C_ne^{i[\mp(\pi/2)n+\arg\Gamma(n+1\mp is)]}Y_n^m(\eta) \tag{10}$$

may be considered as a regular solution for Eq. (2).

### B. Determination of the separation constant and the $C_n$ coefficients

For fixed values of $K$, $R$, $l$, and $|m|$, the separation constant $A_{l|m|}$ can be calculated very easily by use of Kerner's [14] procedure together with Killingbeck's [15] procedure applied to relation (8). These procedures are also detailed in Ref. [16]. The application to the case of $H_eH^{2+}$ is performed: all the values of $A_{l|m|}(R)$ obtained for $K=1$ and for the $s\sigma$, $p\sigma$, and $p\pi$ waves agree totally with those tabulated in Ref. [7]. Once the value of $A_{l|m|}$ is known, and assuming that for a large value of $n$ ($n=N_1$) greater than the series truncation value $N$ we set $C_{N_1+1}=0$ and $C_{N_1}=1$, then all the $C_n$ coefficients down to $C_{|m|}$ are determined by using Miller's [17] backwards recurrence algorithm. The condition $C_n\to C_n/C_{|m|}$ corresponding to an overall normalization is used. Let us note that Ponomarov and Somov [6] and Rankin and Thorson [7] have used the expansion (5) to represent the angular part but, because of the algorithm they adopted to calculate the series coefficients, convergence was poor even for moderate values of $R$ and $K$.

## IV. RADIAL EQUATION

The radial equation (3) has two singularities at $\lambda=\pm1$ and one essential singularity at $\infty$, and the radial Coulomb spheroidal function $\Lambda(\lambda)$ is required to be finite at $\lambda=1$. As $\lambda\to\infty$, $\lambda\to 2r/R$ and $p\lambda\to Kr$ where $r$ is the distance of the electron from the geometric center of the nuclei. $\Lambda(\lambda)$ must have the asymptotic form

$$\lim_{\lambda\to\infty}\Lambda(\lambda)=\frac{\sin[Kr+\sigma\ln(2Kr)+\Delta_{l|m|}]}{r}\ , \tag{11}$$

where $\Delta_{l|m|}$ is the phase shift.

### A. Solution for the radial equation

It is now known [8,10] that there are two linearly independent solutions $\Lambda_\nu(\lambda)$ and $\Lambda_{-\nu-1}(\lambda)$ which satisfy the properties

$$\begin{aligned}&\Lambda_\nu(e^{2i\pi}\lambda)=e^{2i\pi\nu}\Lambda_\nu(\lambda)\ ,\\&\Lambda_{-\nu-1}(e^{2i\pi}\lambda)=e^{-2i\pi(\nu+1)}\Lambda_{-\nu-1}(\lambda)\ .\end{aligned}\tag{12}$$

$\nu=\nu_{l|m|}(K,R)$ is the characteristic exponent and determines the branching character of the solution around $\lambda=\infty$; its value can be real or complex. It is important to notice that the above definition implies that $\nu$ can be replaced by $\nu\pm k$, where $k$ is an arbitrary integer.

We shall consider the well-known expansion over the Legendre functions of the first kind with separated exponent as a regular general solution for Eq. (3):

$$\Lambda^{m(\pm)}(\lambda)=e^{\pm ip\lambda}\sum_{n=-\infty}^{+\infty}d^{m(\pm)}_{\nu+n}P^m_{\nu+n}(\lambda)\ .\tag{13}$$

Indeed, since

$$P^m_{\nu+n}(\lambda)=\frac{\tan(\pi\nu)}{\pi}[Q^m_{\nu+n}(\lambda)-Q^m_{-\nu-n-1}(\lambda)]\tag{14}$$

and since the following relations are satisfied by the Legendre functions of the second kind [18]:

$$\begin{aligned}&Q^m_{-\nu-n-1}(e^{2i\pi}\lambda)=e^{2i\pi\nu}Q^m_{-\nu-n-1}(\lambda)\ ,\\&Q^m_{\nu+n}(e^{2i\pi}\lambda)=e^{-2i\pi(\nu+1)}Q^m_{\nu+n}(\lambda)\ ,\end{aligned}\tag{15}$$

then

$$\Lambda^m_{-\nu-1}(\lambda)=\frac{\tan\pi\nu}{\pi}e^{\pm ip\lambda}\sum_n d^{m(\pm)}_{\nu+n}Q^m_{-\nu-n-1}(\lambda)\tag{16a}$$

and

$$\Lambda^m_\nu(\lambda)=-\frac{\tan\pi\nu}{\pi}e^{\pm ip\lambda}\sum_n d^{m+}_{\nu+n}Q^m_{-\nu-n-1}(\lambda)\tag{16b}$$

are the two independent solutions which satisfy the properties (12). Therefore

$$\Lambda^{m(\pm)}(\lambda)=\Lambda^{m(\pm)}_\nu(\lambda)+\Lambda^{m(\pm)}_{-\nu-1}(\lambda)$$

is a suitable regular solution for Eq. (3).

### B. Recurrence relations

Substituting expression (13) into Eq. (3) gives the following three-term recurrence relations satisfied by the $d^{m(\pm)}_{\nu+n}$ coefficients:

$$\alpha^\pm_{\nu+n}d^{m(\pm)}_{\nu+n-1}+\beta_{\nu+n}d^{m(\pm)}_{\nu+n}+\gamma^\pm_{\nu+n}d^{m(\pm)}_{\nu+n+1}=0\ ,\tag{17}$$

where

$$\begin{aligned}\alpha^\pm_{\nu+n}&=\frac{[q\pm 2ip(\nu+n)](\nu+n-m)}{(2\nu+2n-1)}\\&=\frac{\pm 2ip(\nu+n\mp i\sigma)(\nu+n-m)}{(2\nu+2n-1)}\ ,\end{aligned}$$

$$\beta_{\nu+n}=p^2-A+(\nu+n)(\nu+n+1)\ ,$$

$$\begin{aligned}\gamma^\pm_{\nu+n}&=\frac{[q\mp 2ip(\nu+n+1)](\nu+n+1+m)}{(2\nu+2n+3)}\\&=\frac{\mp 2ip(\nu+n+1\pm i\sigma)(\nu+n+1+m)}{(2\nu+2n+3)}\ ,\end{aligned}$$

and

$$q=R(Z_A+Z_B)\ ,\quad \sigma=\frac{q}{2p}=\frac{(Z_A+Z_B)}{K}\ .$$

Alternative forms of relation (17) are

$$\begin{aligned}&\mathcal{C}^\pm_{\nu+n}=-\alpha^\pm_{\nu+n}/(\beta_{\nu+n}+\gamma^\pm_{\nu+n}\mathcal{C}^\pm_{\nu+n+1})\ ,\\&\mathcal{C}^\pm_{\nu+n}=d^{m(\pm)}_{\nu+n}/d^{m(\pm)}_{\nu+n-1}\ ,\end{aligned}\tag{18a}$$

$$\begin{aligned}&\mathcal{D}^\pm_{\nu+n}=-\gamma^\pm_{\nu+n}/(\beta_{\nu+n}+\alpha^\pm_{\nu+n}\mathcal{D}^\pm_{\nu+n-1})\ ,\\&\mathcal{D}^\pm_{\nu+n}=d^{m(\pm)}_{\nu+n}/d^{m(\pm)}_{\nu+n+1}\ .\end{aligned}\tag{18b}$$

Equation (18a) will be used for $n\geq 0$ and Eq. (18b) for $n\leq 0$; $\nu$ is the correct characteristic exponent if $C^\pm_\nu\mathcal{D}^\pm_{\nu-1}=1$.

The convergence of the recurrent relation (17) and the convergence of the solution (13) will not be developed here since they have been discussed elsewhere [8].

### C. Relations between the $d^{m(\pm)}_{\nu+n}$ expansion coefficients and series representation for the solutions

(a) Since $P^{(m)}_{\nu+n}(\lambda)=P^m_{-\nu-n-1}(\lambda)$, the substitution $\nu+n\rightarrow-\nu-1-n$ in the solution (13) leads to

$$d^{m(\pm)}_{\nu+n}=d^{m(\pm)}_{-\nu-n-1}\ ,\tag{19}$$

which can also be obtained from Eq. (17) when performing the same substitution.

(b) In the same way, the relation

$$P^m_{\nu+n}(\lambda)=\frac{\Gamma(1+\nu+n+m)}{\Gamma(1+\nu+n-m)}P^{-m}_{\nu+n}(\lambda)$$

leads to

$$d^{-m(\pm)}_{\nu+n}=\frac{\Gamma(1+\nu+n+m)}{\Gamma(1+\nu+n-m)}d^{m(\pm)}_{\nu+n}\ .\tag{20}$$

(c) The matrix, whose elements are the coefficients $\alpha^+_{\nu+n}$, $\beta_{\nu+n}$, and $\gamma^+_{\nu+n}$ in Eq. (17), can be modified to the matrix whose elements are $\alpha^-_{\nu+n}$, $\beta_{\nu+n}$, and $\gamma^-_{\nu+n}$ by setting, for instance,

$$d^{m(+)}_{\nu+n}=(-1)^n\frac{\Gamma(\nu+1+i\sigma)}{\Gamma(\nu+1-i\sigma)}\frac{\Gamma(\nu+n+1-i\sigma)}{\Gamma(\nu+n+1+i\sigma)}d^{m(-)}_{\nu+n}\ .\tag{21}$$

and since

$$\begin{aligned}&\frac{\Gamma(\nu+n+1-i\sigma)}{\Gamma(\nu+n+1+i\sigma)}\frac{\Gamma(\nu+1+i\sigma)}{\Gamma(\nu+1-i\sigma)}\\&\qquad=\frac{\Gamma(-\nu-n-i\sigma)}{\Gamma(-\nu-n+i\sigma)}\frac{\Gamma(-\nu+i\sigma)}{\Gamma(-\nu-i\sigma)}\end{aligned}$$

the relation (19) is satisfied by the $d^{m(-)}_{\nu+n}$ coefficients.

(d) From Eq. (17),

$$(d_{\nu+n}^{m(+)})^*=d_{\nu^*+n}^{m(-)}\ ,\quad (d_{\nu}^{m(+)})^*=d_{\nu^*}^{m(-)}\ . \tag{22}$$

(e) The recurrence relation (17) can be modified so that the $(\pm)$ signs as well as the sign of the magnetic quantum number $m$ are removed on setting

$$d_{\nu+n}^{m(\pm)}=(\pm 1)^n\left\{\frac{\Gamma(\nu+n+1\mp i\sigma)}{\Gamma(\nu+n+1\pm i\sigma)}\frac{\Gamma(\nu+1\pm i\sigma)}{\Gamma(\nu+1\mp i\sigma)}\right\}^{1/2}\times\left\{\frac{\Gamma(\nu+n+1-m)}{\Gamma(\nu+n+1+m)}\frac{\Gamma(\nu+1+m)}{\Gamma(\nu+1-m)}\right\}^{1/2}q_{\nu+n}\ , \tag{23}$$

$$d_{\nu}^{m(\pm)}=q_{\nu}=1\ .$$

Then the coefficients $q_{\nu+n}$ satisfy the relation

$$a_{\nu+n}q_{\nu+n-1}+\beta_{\nu+n}q_{\nu+n}+c_{\nu+n}q_{\nu+n+1}=0\ , \tag{24}$$

where

$$a_{\nu+n}=-2p\frac{\{[(\nu+n)^2-m^2][(\nu+n)^2+\sigma^2]\}^{1/2}}{2\nu+2n-1}\ ,$$

$$c_{\nu+n}=-2p\frac{\{[(\nu+n+1)^2-m^2][(\nu+n+1)^2+\sigma^2]\}^{1/2}}{2\nu+2n+3}\ .$$

(f) Series expansions. Finally, the expansion of the hypergeometric series representation for the Legendre functions of the second kind, i.e.,

$$Q_{-\nu-n-1}^{m}(\lambda)=\left[\frac{\lambda+1}{\lambda-1}\right]^{m/2}e^{im\pi}2^{-\nu-n-1}\frac{\Gamma(-\nu-n)\Gamma(-\nu-n-m)}{\Gamma(-2\nu-2n)}(1+\lambda)^{\nu+n}\times F\left[-\nu-n-m,-\nu-n,-2\nu-2n;\frac{2}{1+\lambda}\right] \tag{25}$$

and the use of relations (20) and (19) lead to

$$\Lambda_{\nu}^{m(\pm)}(\lambda)=e^{\pm ip\lambda}\left[\frac{\lambda+1}{\lambda-1}\right]^{m/2}\times(1+\lambda)^{\nu}\sum_{t=-\infty}^{+\infty}a_{\nu}(t)(1+\lambda)^{t}\ , \tag{26a}$$

where

$$a_{\nu}(t)=\frac{2^{-\nu-t}}{\Gamma(1+\nu+t)\Gamma(1+\nu+t+m)}\times\sum_{k=0}\frac{(-1)^k}{k!}d_{\nu+t+k}^{-m(\pm)}\Gamma(1+2\nu+2t+k)$$

or

$$a\nu(t)=\frac{2^{-\nu-t}\Gamma(1+2\nu+2t)}{\Gamma(1+\nu+t)\Gamma(1+\nu+t+m)}\times d_{\nu+t}^{m(\pm)}\left[1+\sum_{k=1}\frac{(-1)^k}{k!}\frac{d_{\nu+t+k}^{-m(\pm)}}{d_{\nu+t}^{-m(\pm)}}\prod_{j=1}^{k}(2\nu+2t+j)\right].$$

Similarly, we get

$$\Lambda_{-\nu-1}^{m(\pm)}=e^{\pm ip\lambda}\left[\frac{\lambda+1}{\lambda-1}\right]^{m/2}\times(1+\lambda)^{-\nu-1}\sum_{t=-\infty}^{+\infty}a_{-\nu-1}(t)(1+\lambda)^{t}\ . \tag{26b}$$

### D. Determination of the characteristic exponent $\nu$ and the $d_{\nu+n}^{m(\pm)}$ coefficients

$\mathbf{\Lambda}^{m(+)}(\lambda)$ being a solution of the linear equation (3), then $[\mathbf{\Lambda}^{m(+)}(\lambda)]^*$ is also a solution. Using relation (21), we can write

$$[\mathbf{\Lambda}^{m(+)}(\lambda)]^*=e^{-ip\lambda}\sum_{n=-\infty}^{+\infty}d_{\nu^*+n}^{m(-)}P_{\nu^*+n}^{m}(\lambda)\ ,$$

which is of the form of $\mathbf{\Lambda}^{m(-)}(\lambda)$. This implies that either

$$\nu^*=\nu\pmod k$$

or

$$\nu^*=-\nu-1\pmod k\ . \tag{27}$$

Consequently, $\nu$ can be real,

$$\nu=b\pmod k\ , \tag{27a}$$

or complex,

$$\nu=-\tfrac{1}{2}\pm ib\pmod k\ , \tag{27b}$$

$$\nu=\pm ib\pmod k\ . \tag{27c}$$

The possible values for $\nu=\nu_{l|m|}(K,R)$ given $A$ must satisfy the condition to obtain a nontrivial solution for Eq. (17), i.e., the infinite determinant $\Delta(\nu)$ of the coefficients of $d_{\nu+n}^{m(\pm)}$ in Eq. (17) must be zero for self-consistency; starting with $R=R_1$, $R_1\leq 1$, the roots of $\Delta(\nu)$ may be obtained with relative accuracy by considering its expansion around the central term $\Delta_{1,1}(\nu)=\beta_{\nu}$. The truncated determinant $\Delta_{2j+1,2j+1}(\nu)$ equal to $\Delta(\nu)$ with all rows and columns beyond $j+1$ and $-j-1$ deleted is a ratio of two polynomials $\mathcal{R}_j(\nu)/\mathcal{Q}_j(\nu)$; $\mathcal{R}_j(\nu)$ is of degree $2(3j+1)$ in $\nu$ [or $(3j+1)$ in $\nu(\nu+1)$]. By finding the roots of $\mathcal{R}_j(\nu)$ successively for $j=2,3,\ldots$, the root that converges to the required form can be considered as a first approximate value of $\nu$. This can be achieved easily

by computing $\Delta_{2j+1,2j+1}(\nu)$ in a formal language such as, in this case, Macsyma implemented on an Apollo 3500. $\mathcal{R}_j(\nu)$, as well as the corresponding roots, are found in a straightforward way. Then the starting value for $\nu$ is improved in the following manner: the $d_{\nu+n}^{m(\pm)}$ coefficients are set equal to zero for $n>N$ and $n<-N$, where $N$ is an integer sufficiently large so that the good convergence of the solution is guaranteed; the relation (18a) for $n=N$ down to $n=0$ and (18b) for $n=-N$ up to $n=-1$ are used to compute the $\mathcal{C}_{\nu+n}^{\pm}$ and the $\mathcal{D}_{\nu+n}^{\pm}$ coefficients. $\nu$ is then adjusted so that $\mathcal{D}_{\nu-1}^{\pm}C_{\nu}^{\pm}=1$. Then $\nu=\nu(K,R)$ can be used as a starting value for $R_2=R_1+\Delta R$. Once $\nu$ is determined, on setting $d_{\nu}^{m(\pm)}=d_{-\nu-1}^{m(\pm)}=1$ to fix the normalization for the solutions, the $d_{\nu+n}^{m(\pm)}$ $(n>0)$ and the $d_{\nu+n}^{m(\pm)}$ $(n<0)$ expansion coefficients are easily obtained from $\mathcal{C}_{\nu+n}^{(\pm)}$ and $\mathcal{D}_{\nu+n}^{(\pm)}$, respectively.

This procedure to find a starting value for $\nu$ differs from the one proposed by Greeland and Greiner [18]. They used properties of functions of complex variables together with the procedure used in the determination of the characteristic exponent for the Mathieu functions [18] to show that $\cos 2\pi\nu$ is real, which confirms that $\nu$ has one of the predicted forms.

### E. Asymptotic behavior and phase shift

In order to obtain the asymptotic behavior of the solution (13), it is more adequate to use an equivalent expansion representation for $\Lambda_{\nu}^{m(\pm)}(\lambda)$ $[\Lambda_{-\nu-1}^{m(\pm)}(\lambda)]$ whose asymptotic behavior is known. Indeed, the following expansion $\mathcal{S}_{\nu}^{m}(\lambda)$ $[\mathcal{S}_{-\nu-1}^{m}(\lambda)]$, which is closely related to the expansion introduced by Abramov and co-workers [10,11] and Greenland and Greiner [8], can be used as an alternative solution for Eq. (3):

$$\mathcal{S}_{\nu}^{m}(\lambda)=\left[\frac{\lambda+1}{\lambda-1}\right]^{m/2}\sum_{n=-\infty}^{+\infty}k_{\nu+n}^{m}S_{\nu+n}^{m}(\lambda)\ , \tag{28}$$

where

$$S_{\nu+n}^{m}(\lambda)=e^{-ip(\lambda+1)}[2ip(\lambda+1)]^{\nu+n}\frac{\Gamma(\nu+n+1+i\sigma)}{\Gamma(2\nu+2n+2)}$$

$$\times M(\nu+n+1+i\sigma,2\nu+2n+2,2ip(\lambda+1))\ .$$

$M(a,b,2ip(\lambda+1))$ is the confluent hypergeometric function of the first kind.

When substituting $\mathcal{S}_{\nu}^{m}(\lambda)$ into Eq. (3), the coefficients $k_{\nu+n}^{m}$ involved in this representation have the advantage of satisfying the difference equation that coincides with Eq. (17) for the $d_{\nu+n}^{m(+)}$ (see Appendix) and we can choose to set

$$k_{\nu+n}=d_{\nu+n}^{m(+)}\ . \tag{29}$$

After replacing the confluent hypergeometric function in Eq. (28) by its expansion series in powers of $(1+\lambda)$, the expression for $\mathcal{S}_{\nu}^{m}(\lambda)$ is written as

$$\mathcal{S}_{\nu}^{m}(\lambda)=e^{-ip\lambda}\left[\frac{\lambda+1}{\lambda-1}\right]^{m/2}\sum_{t=-\infty}^{+\infty}b_{\nu}(t)(1+\lambda)^{\nu+t}\ , \tag{30}$$

where

$$b_{\nu}(t)=e^{-ip}(2ip)^{\nu+t}\Gamma(1+\nu+t+i\sigma)\times\sum_{k=0}^{\infty}\frac{1}{k!}\frac{d_{\nu+t-k}^{m(+)}}{\Gamma(2+2\nu+2t-k)}$$

or

$$b_{\nu}(t)=e^{-ip}(2ip)^{\nu+t}\frac{\Gamma(1+\nu+t+i\sigma)}{\Gamma(2+2\nu+2t)}\times d_{\nu+t}^{m(+)}\left[1+\sum_{k=1}^{\infty}\frac{1}{k!}\frac{d_{\nu+t-k}^{m(+)}}{d_{\nu+t}^{m(+)}}\times\prod_{j=1}^{k}(2+2\nu+2t-j)\right]\ .$$

Matching the above expansion (30) with the solution (26a) leads to

$$\Lambda_{\nu}^{m(-)}(\lambda)=A_{\nu}\mathcal{S}_{\nu}^{m}(\lambda)\ , \tag{31}$$

where, whatever the value of the running index $t$,

$$A_{\nu}\left[=\frac{a_{\nu}(t)}{b_{\nu}(t)}\right]=\text{const}\ .$$

Then choosing $t=0$,

$$A_{\nu}=\frac{e^{ip}}{(4ip)^{\nu}}\frac{\Gamma(1+2\nu)\Gamma(2+2\nu)}{\Gamma(1+\nu+i\sigma)\Gamma(1+\nu)\Gamma(1+\nu+m)}\tau_{\nu}\ ,$$

where

$$\tau_{\nu}=\frac{1+\sum_{\kappa=1}^{\infty}\frac{(-1)^k}{k!}\frac{d_{\nu+k}^{-m(-)}}{d_{\nu}^{-m(-)}}\prod_{j=1}^{k}(2\nu+j)}{1+\sum_{k=1}^{\infty}\frac{1}{k!}\frac{d_{\nu-k}^{m(+)}}{d_{\nu}^{m(+)}}\prod_{j=1}^{k}(2+2\nu-j)}\frac{d_{\nu}^{-m(-)}}{d_{\nu}^{m(+)}}\ .$$

Now we can write the equivalent expression for the solution $\Lambda^{m(-)}(\lambda)$:

$$\Lambda^{m(-)}(\lambda)=A_{\nu}\mathcal{S}_{\nu}^{m}(\lambda)+A_{-\nu-1}\mathcal{S}_{-\nu-1}^{m}(\lambda)\ . \tag{32}$$

The asymptotic form of $\mathcal{S}_{\nu}^{m}(\lambda)$ [and of $\mathcal{S}_{-\nu-1}^{m}(\lambda)$] is obtained from expansion (28), after replacing the confluent hypergeometric function by its well-known asymptotic form:

$$\lim_{\lambda\to\infty}\mathcal{S}_{\nu}^{m}(\lambda)=\frac{e^{-(\pi/2)\sigma}}{2ip(\lambda+1)}\left\{\alpha_{\nu}e^{-i\{p(\lambda+1)+\sigma\ln[2p(\lambda+1)]\}}+\beta_{\nu}e^{+i\{p(\lambda+1)+\sigma\ln[2p(\lambda+1)]\}}\right\} \tag{33}$$

where

$$\beta_{\nu}=\sum_{n}d_{\nu+n}^{m(+)}$$

and

$$\alpha_{\nu}=\sum_{n}e^{i\pi(\nu+n+1)}\frac{\Gamma(\nu+n+1+i\sigma)}{\Gamma(\nu+n+1-i\sigma)}d_{\nu+n}^{m(+)}\ ,$$

or from Eq. (21),

$$\alpha_\nu = e^{i\pi(\nu+1)}\frac{\Gamma(\nu+1+i\sigma)}{\Gamma(\nu+1-i\sigma)}\sum_n d_{\nu+n}^{m(-)} .$$

Let us note that because of relation (19),

$$\beta_{-\nu-1}=\beta_\nu , \quad \alpha_{-\nu-1}=e^{-i\pi(2\nu+1)}\frac{\sin\pi(\nu+i\sigma)}{\sin\pi(\nu-i\sigma)}\alpha_\nu \tag{34}$$

and

$$\frac{\beta_\nu}{\alpha_\nu}=e^{-i\pi(\nu+1)}\frac{\Gamma(\nu+1-i\sigma)}{\Gamma(\nu+1+i\sigma)}\frac{\sum_n d_{\nu+n}^{m(+)}}{\sum_n d_{\nu+n}^{m(-)}} . \tag{35}$$

Then

$$\lim_{\lambda\to\infty}\Lambda^{m(-)}(\lambda) = \frac{e^{-(\pi/2)\sigma}}{2ip(\lambda+1)}(f(\nu)\cos\{p(\lambda+1)+\sigma\ln[2p(\lambda+1)]\} + ig(\nu)\sin\{p(\lambda+1)+\sigma\ln[2p(\lambda+1)]\}) \tag{36}$$

where

$$f(\nu)=A_\nu(\beta_\nu+\alpha_\nu)+A_{-\nu-1}(\beta_{-\nu-1}+\alpha_{-\nu-1}) ,$$
$$g(\nu)=A_\nu(\beta_\nu-\alpha_\nu)+A_{-\nu-1}(\beta_{-\nu-1}-\alpha_{-\nu-1}) .$$

An alternative form of the above limit is

$$\lim_{\lambda\to\infty}\Lambda^{m(-)}(\lambda)=\frac{B\sin\{p(\lambda+1)+\sigma\ln[2p(\lambda+1)+\theta]\}}{r} = \frac{B\sin[Kr+\sigma\ln(2Kr)+\theta+p]}{r} , \tag{37}$$

where

$$B=\frac{e^{-(\pi/2)\sigma}}{2K}\{[g(\nu)-f(\nu)][g_\nu+f(\nu)]\}^{1/2}$$

represents the normalization factor and where

$$\tan(\theta)=-i\frac{f(\nu)}{g(\nu)} . \tag{38}$$

The phase shift $\Delta_{l|m|}$ in Eq. (11) is related to $\theta$ by $\Delta_{l|m|}=\theta+p$.

The exponential form of $\tan\theta$ and the definitions of $f(\nu)$ and $g(\nu)$ lead to

$$e^{2i\theta}=-\frac{A_\nu\beta_\nu+A_{-\nu-1}\beta_{-\nu-1}}{A_\nu\alpha_\nu+A_{-\nu-1}\alpha_{-\nu-1}} = -\frac{\beta_\nu}{\alpha_\nu}\frac{1+\rho_\nu}{1+\frac{\alpha_{-\nu-1}}{\alpha_\nu}\rho_\nu} ,$$

where $\rho_\nu=A_{-\nu-1}/A_\nu$. After replacing $\rho_\nu$, $\beta_\nu$ $(=\beta_{-\nu-1})$, $\alpha_\nu$, and $\alpha_{-\nu-1}$ by their expressions in terms of $\nu$, we finally obtain the expression of the phase shift through $\nu$ and through the $d_{\nu+n}^{m(\pm)}$ coefficients:

$$e^{2i\theta}=e^{-i\pi\nu}\frac{\Gamma(\nu+1-i\sigma)}{\Gamma(\nu+1+i\sigma)}\frac{\sum_n d_{\nu+n}^{m(+)}}{\sum_n d_{\nu+n}^{m(-)}} \times\frac{1+\rho_\nu}{1+e^{-i\pi(2\nu+1)}\frac{\sin\pi(\nu+i\sigma)}{\sin\pi(\nu-i\sigma)}\rho_\nu} , \tag{39}$$

where

$$\rho_\nu=-ie^{i\pi\nu}\frac{\Gamma(\nu+1+i\sigma)}{\Gamma(-\nu+i\sigma)}\left[\frac{p}{4}\right]^{2\nu+1} \times\frac{(-1)^m\pi^2}{(\nu+\frac{1}{2})^2\cos^2\pi\nu} \times\frac{\Gamma(\nu+m+1)\Gamma(\nu-m+1)}{\Gamma^4(\nu+\frac{1}{2})\Gamma^2(\nu+1)}\frac{\tau_{-\nu-1}}{\tau_\nu} .$$

Expression (39) is an extension to the whole range for $R$ and $p$ of the asymptotic form in the united-atom approximation proposed by Abramov *et al.* [11]. It is easily verified that in the united-atom limit, $\theta$ tends to the appropriate phase shift: $\arg\Gamma(l+1-i\sigma)$; $\theta$ is related to the

TABLE I. Separation constant, characteristic exponent, and phase shift for the $s\sigma$ state of $H_2^+$.

| | $K=1,\ l=0,\ m=0$ | | | $K=5,\ l=0,\ m=0$ | | |
|---|---|---|---|---|---|---|
| $R$ (a.u.) | $A$ | $\nu$ | $\Delta=\theta+p$ | $A$ | $\nu$ | $\Delta=\theta+p$ |
| 0.5 | 0.020 775 | −0.174 332 5 | −0.3613 | 0.486 518 | 0.821 506 78 | −0.0366 |
| | | | | | | −0.0366[a] |
| 1 | 0.082 415 | −0.5+$i$(0.428 067) | −0.6782 | 1.622 380 | −0.5+$i$(0.531 69) | −0.3133 |
| | | | −0.6782[b] | | | |
| 2 | 0.319 000 | −0.5+$i$(0.869 500) | −1.2413 | 4.195 130 | −0.5+$i$(1.663 556) | −0.6233 |
| | | | −1.2375[b] | | | −0.6320[b] |
| 3 | 0.680 575 | −0.5+$i$(1.101 183) | −1.7082 | 6.719 161 | −0.5+$i$(3.020 378) | −0.7953 |
| 4 | 1.127 734 | −0.5+$i$(1.256 255) | −2.1011 | 9.228 306 | −0.5+$i$(4.459 031) | −0.8704 |
| | | | −2.1080[b] | | | |
| 5 | 1.622 380 | −0.5+$i$(1.380 605) | −2.4354 | 11.733 215 | −0.5+$i$(5.935 768) | −1.0464 |

[a]Value obtained by the numerical procedure of Ponomarev and Somov and by asymptotic formula of Abramov *et al.* [11].
[b]Values calculated by the algorithm of Nakamura and Takagi [19].

phase shift $\Delta_{mq}^{PS}$ reported by Ponomarev and Somov [6] and the phase shift $\delta_R$ reported by Ramkin and Thorson [7] by $\theta=\Delta_{mq}^{PS}-p-l\pi/2$ and $\theta=\delta_R-p-\sigma\ln(2)$, respectively.

### F. Applications and discussion

The procedure presented in Sec. IV D is tested first for the cases of the $s\sigma$, $p\sigma$, and $d\sigma$ states of $H_2^+$ for $K=(2)^{1/2}$ and $R\leq 4$ a.u. All the corresponding values of $\nu$ reported in Ref. [8] are found again. Next, $K$ is increased from 1 to 5 and the calculation repeated for the $s\sigma$ state of $H_2^+$ in the range $0.5\leq R\leq 5$ a.u. The results are shown in Table I. For moderate values of the parameter $p$ ($p\leq 7$), to evaluate the initial value $\nu_i$, it is found that there is no need for the index $j$ involved in the truncated determinant $\Delta_{2j+1,2j+1}(\nu)$ to go beyond $j=7$; but, as $p$ increases, determining $\nu_i$ requires larger values of $j$ and therefore depends on the computer's capacity to find the roots of $\mathcal{R}_j(\nu)$. Beyond this capacity, for the inter-center distance $R_2=R_1+\Delta R$, $\nu(R_1)$ is used as the initial value $\nu_i$ for $\nu(R_2)$. In all cases, the value of the characteristic exponent is obtained by scanning $\nu_i$ until $\mathcal{D}_{\nu-1}^{\pm}\mathcal{C}_{\nu}^{\pm}=1$ ($|\mathcal{D}_{\nu-1}^{\pm}\mathcal{C}_{\nu}^{\pm}-1|\leq 10^{-5}$). The complex $\Gamma(z)$ functions involved in formula (39) are computed according to the series expansion in powers of $z$ for $1/\Gamma(z)$ when $|z|\leq 2$ and according to Stirling's formula when $|z|\geq 2$, the accuracy of the values obtained being adequate for this need. Finally, in order to be able to compare values of the phase shifts issued from relation (39) with those obtained from a numerical procedure, the case of the $s\sigma$, $p\sigma$, and $p\pi$ states of $H_eH^{2+}$ seems appropriate since comparative numerical values are available. For $K=1$ and for the selected values of $l$, $m$, and $R$, Table II displays the values of the characteristic exponent and the phase shifts which are compared with those found by Rankin and Thorson [7]. Results agree very well.

In conclusion, the process to obtain the characteristic exponent is quite simple; once $\nu$ is determined, it leads to an analytic expression for the radial wave functions and allows the determination of the phase shifts which are involved in the calculation of the scattering cross sections of electrons on two Coulomb centers. The analytic form of the wave functions may be useful to calculate matrix elements between bound and continuum states, especially for large values of $p$. Indeed, due to the oscillating nature of the wave functions, numerical calculation of these matrix elements becomes difficult as $p$ increases [20].

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### APPENDIX

Recurrence relations for the $S_{\nu}^{m}(\lambda)$ are obtained by use of relations between the confluent hypergeometric functions given in Ref. (18), Sec. 13.4, p. 506, and after setting $z=ip(\lambda+1)$:

$$\nu(\nu+1)S_{\nu}^{m}(\lambda)=z\left\{\frac{(\nu+i\sigma)(\nu+1)}{(2\nu+1)}S_{\nu-1}^{m}(\lambda)-isS_{\nu}^{m}(\lambda)-\frac{(\nu+1-i\sigma)\nu}{(2\nu+1)}S_{\nu+1}^{m}(\lambda)\right\}$$

TABLE II. Characteristic exponents and comparative values of the phase shifts for $K=1$ calculated by formula (39) and by Rankin and Thorson's algorithm for the $s\sigma$, $p\sigma$, and $p\pi$ waves of $H_eH^{2+}$. Note that $\delta=\theta+p+\sigma\ln 2$. The $\delta_R$ values are printed directly below the $\delta$ values for ease of comparison.

| $R$ (a.u.) | $s\sigma(l=0,m=0)$ | | $p\sigma(l=1,m=0)$ | | $p\pi(l=1,m=1)$ | |
|---|---|---|---|---|---|---|
| | $\nu$ | $\delta$ | $\nu$ | $\delta$ | $\nu$ | $\delta$ |
| | | $\delta_R$ | | $\delta_R$ | | $\delta_R$ |
| 1 | $-0.5+i(0.686\,978)$ | 0.2799 | 0.794 52 | 4.8557 | $i(0.158\,450)$ | 4.2065 |
| | | 0.2798 | | 4.8578 | | 4.2061 |
| 2 | $-0.5+i(1.153\,69)$ | −0.3537 | 0.878 73 | 4.6292 | $i(0.751\,94)$ | 3.7688 |
| | | −0.7192[a] | | 4.6314 | | 3.7688 |
| 3 | $-0.5+i(1.412\,46)$ | −0.9241 | $-0.5+i(0.662\,23)$ | 4.2210 | $i(1.159\,98)$ | 3.3512 |
| | | −0.9215 | | 4.2276 | | 3.3510 |
| 4 | $-0.5+i(1.560\,11)$ | −1.4174 | $-0.5+i(1.100\,06)$ | 3.8248 | $i(1.451\,96)$ | 2.9961 |
| | | −1.4079 | | 3.8245 | | 2.9659 |
| 5 | $-0.5+i(1.613\,96)$ | −1.8464 | $-0.5+i(1.380\,06)$ | 3.4536 | $i(1.680\,19)$ | 2.6108 |
| | | −1.8466 | | 3.4534 | | 2.6106 |
| 6 | $-0.5+i(1.537\,62)$ | −0.2423 | $-0.5+i(1.585\,18)$ | 3.2135 | $i(1.869\,47)$ | 2.2822 |
| | | −2.2425 | | 3.0975 | | 2.2821 |
| 7 | $-0.5+i(0.444\,72)$ | −2.5977 | $-0.5+i(1.735\,46)$ | 2.7509 | $i(2.035\,00)$ | 1.9781 |
| | | −2.5983 | | 2.7507 | | 1.9780 |
| 8 | $-0.5+i(1.766\,43)$ | −2.9170 | $-0.5+i(1.836\,78)$ | 2.3833 | $i(2.188\,0)$ | 1.6962 |
| | | −2.9172 | | 2.4131 | | 1.6964 |
| 9 | $-0.5+i(2.070\,63)$ | −3.2036 | $-0.5+i(1.889\,97)$ | 2.0892 | $i(2.340\,02)$ | 1.4357 |
| | | −3.2040 | | 2.0890 | | 1.4355 |
| 10 | $-0.5+i(2.257\,73)$ | −3.4634 | $-0.5+i(1.890\,15)$ | 1.7834 | $i(2.495\,53)$ | 1.1947 |
| | | −3.4634 | | 1.7835 | | 1.1935 |

[a]We believe that there must be a misprint for this value in Rankin and Thorson's table [7].

and

$$(2\nu+1)\frac{dS_\nu^m(\lambda)}{dz}=[(\nu+i\sigma)S_{\nu-1}^m(\lambda) +(\nu+1-i\sigma)S_{\nu+1}^m(\lambda)] .$$

The $S_\nu^m(\lambda)$ functions satisfy the differential equation

$$\left[z^2\frac{d^2}{dz^2}+2z\frac{d}{dz}-z^2-2i\sigma z-\nu(\nu+1)\right]S_\nu^m(\lambda)=0$$

and the radial equation (3) can be transformed as

$$\left\{\left[z^2\frac{d^2}{dz^2}+2z\frac{d}{dz}-z^2-2i\sigma z-\nu(\nu+1)\right] +\frac{ip}{z-2ip}\left[\nu(\nu+1)\frac{(z-2ip)}{ip}-2i\sigma z+\frac{(p^2-A)z}{ip} +2(1-m)z\frac{d}{dz}\right]\right\}\Lambda(\lambda)=0 .$$


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